

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 87200347.0

(51) Int. Cl.⁴ C11D 3/39

(22) Date of filing: 26.02.87

(30) Priority: 07.03.86 US 837613

(43) Date of publication of application:
16.09.87 Bulletin 87/38

(84) Designated Contracting States:
CH DE ES FR GB IT LI NL SE

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(54) Detergent bleach composition, bleaching compositions and bleach activators.

(57) Bleaching agent compositions and detergent bleach formulations containing them comprise effective amounts of (a) a peroxide compound having a bleaching action; and (b) a catalyst for the bleaching action of the peroxide compound, said catalyst comprising a water-soluble complex of manganese (III) with a multidentate ligand which imparts both hydrolytic and oxidative stability to the Mn(III). The amount of complexing agent in the catalyst that supplies the multidentate ligand to form the complex is such that the molar ratio of complexing agent to manganese is at least about 1:1, preferably 10:1 or greater. Suitable complexing agents are hydroxycarboxylic acids containing 5 or more carbon atoms and the salts, lactones, acid esters, ethers and boric esters thereof.

DETERGENT BLEACH COMPOSITIONS, BLEACHING COMPOSITIONS AND BLEACH ACTIVATORS

This invention relates to detergent bleach formulations containing a bleaching agent, that are suitable for washing fabrics and removing stains on fabrics. The bleaching agent can be hydrogen peroxide or a water-soluble peroxide adduct, e.g. one or more inorganic persalts which liberate hydrogen peroxide in aqueous solution such as metal perborates, percarbonates, and persulfates.

5 Peroxide bleaching agents for use in laundering have been known for many years. Such agents are effective in removing stubborn stains from clothing such as tea, fruit and wine stains. However, the efficacy of peroxide bleaching agents drops off sharply below 60°C. Consequently, bleach catalysts or heavy metal bleach activators have been employed to achieve satisfactory bleaching at the lower wash temperatures needed to avoid scalding of laundry workers and household consumers of laundry detergents. However, 10 heavy metal catalysts, for example as described in U.S. Patent 3,156,654, tend to promote the decomposition of hydrogen peroxide by reaction mechanisms which do not contribute to the desired bleaching effect, with consequent loss of bleaching performance. To control such loss of hydrogen peroxide, sequestrants for the heavy metals, such as ethylene diamine tetraacetic acid (EDTA) and diethylene triamine pentaacetic acid (DEPTA) or their salts have been added to detergent bleach formulations. Unfortunately, sequestrants 15 can also inhibit bleaching catalysis, so that a balance is needed to maximize bleaching action while minimizing non-bleaching decomposition of the peroxide.

A related, but separate problem is the hydrolytic instability of heavy metal ions under normal (alkaline) wash conditions. Thus, in the absence of sequestering agents, heavy metal hydroxides will precipitate from solution and deposit themselves on the fabrics being laundered. Another problem is oxidative instability of 20 heavy metal ions in the presence of certain non-peroxide oxidizing agents. For example, in the presence of hypochlorite, an oxidizing chlorine bleach which fastidious consumers may add to the wash water in the belief that it supplements the action of the peroxide bleaching agents in the detergent formulation, insoluble heavy metal oxides can form and become deposited on the fabrics. This can happen even in the presence of sequestering agents, which themselves are often susceptible to undesirable oxidation by hypochlorite. In 25 the case of manganese, the presence of peroxide oxidizing agents can already promote undesirable oxidation to insoluble brown manganese dioxide (MnO_2).

Therefore, for a heavy metal to be useful as a bleach catalyst in a detergent bleach formulation, the heavy metal must not unduly promote peroxide decomposition by non-bleaching pathways and must be hydrolytically and oxidatively stable. The patent literature discusses the use of chelating agents to impart 30 both hydrolytic and oxidative stability to the metal centre. Thus, European Patent Application N° 0124341 describes the use of hydroxycarboxylic acids as "bleaching auxiliaries" to provide hydrolytic and oxidative stability to ferrous and ferric ions in solution. U.S. Patent 4,478,733 discloses the use of $Mn(II)$ as a peroxide bleach catalyst in detergent compositions containing perborate, aluminosilicate and orthophosphate over the temperature range 20°-60°C. Likewise, U.S. Patent 4,430,243 indicates that manganese(III) activates 35 perborate bleaching in a detergent formulation. However, none of the prior art provides a heavy metal-based bleach catalyst that is entirely free of the foregoing drawbacks.

EP-A-0141470 discloses manganese(II) cation bound to various ligands and provided with a protective coating to improve stability against discolouration in persalt-containing detergent compositions.

Accordingly, it is an object of the present invention to provide new, improved detergent bleach 40 formulations.

Another object of the invention is to provide aqueous laundry wash media containing new improved detergent bleach formulations.

Another object of the invention is to provide new, improved bleaching agent compositions for use in detergent formulations.

45 Another object is to provide a new system for catalyzing the action of bleaching agent compositions.

Yet another object is to provide a method of producing a new system for catalyzing the action of bleaching agent compositions.

These and other objects of the invention, as well as a further understanding of the features and advantages thereof, can be had from the following description and claims.

50 The foregoing objects are achieved according to the present invention which provides novel peroxide bleach catalyst, promoter or activator systems for use in laundry detergent and/or bleaching applications. The bleach catalysts or activators are based on tripositive manganese ion, $Mn(III)$, and are safe to both the consumer and the environment, while providing improved bleaching activity over the entire ranges of wash temperatures, soil loads and water hardnesses encountered in laundering of clothing and other articles. In addition, the $Mn(III)$ -based catalysts described herein are resistant to both hydrolysis and oxidation, thus

providing a significant improvement in stability over peroxide bleach catalysts based on dipositive manganese ion, $Mn(II)$. In addition to increasing peroxide bleaching efficacy, the bleach promoters or catalysts of the invention actively inhibit the undesirable peroxide decomposition that occurs in the presence of other manganese species independently of bleaching, thus optimizing bleaching performance for any level of peroxide bleach dosage and minimizing the amount of peroxide bleach necessary to achieve satisfactory bleaching. The invention also provides a peroxide bleach catalyst that is stable to oxidants such as hypochlorite which would otherwise cause the formation of MnO_2 , which can form deposits upon and stain fabrics.

- In one particular aspect, the invention provides a detergent bleach formulation comprising
- (a) one or more surface-active agents selected from the group consisting of nonionic, anionic, cationic and zwitterionic detergents;
 - (b) a detergency builder; and
 - (c) a bleaching agent containing
 - (i) one or more peroxide compounds having a bleaching action, and
 - (ii) a catalyst for the bleaching action of the peroxide compound(s), comprising a water-soluble complex of manganese(III) and a multidentate ligand derived from a complexing agent, said catalyst containing sufficient ligand-supplying complexing agent such that the molar ratio of complexing agent to $Mn(III)$ is at least about 1:1.

The composition can be formulated by combining effective amounts of the components (a), (b) and (c)-(i) and (ii) as substantially dry solids. The term "effective amounts" as used herein means that the ingredients are present in quantities such that each of them is operative for its intended purpose when the resulting mixture is combined with water to form an aqueous medium which can be used to wash clothes, fabrics and other articles. In particular, the composition can be formulated to contain a surface-active agent in an amount of from about 2% to about 50% by weight, preferably about 5% to 30%, of the composition; from about 1% to about 85% by weight, preferably about 5% to 50%, detergent builder; and from about 5% to about 30% by weight, preferably about 15% to 25%, peroxide compound.

The catalyst component is a novel feature of the invention. The effective level of the catalyst component, expressed in terms of parts per million (ppm) of $Mn(III)$ in the aqueous wash liquor or solution, ranges from 0.05 ppm to 4 ppm, preferably 0.1 ppm to 2.5 ppm. Above 4 ppm, the wasteful manganese-catalyzed peroxide decomposition pathway becomes dominant. When the detergent bleach composition of the invention is used at concentrations in the wash water of about 2 g/l or 0.2% by weight normally employed by consumers in the United States, this corresponds to a manganese content in the detergent bleach composition of 0.0025% to 0.2% by weight, preferably 0.005 to 0.125% by weight, based on the total weight of the detergent bleach composition. When used at the typical European dosages of 5-6 g/l or 0.5-0.6%, this corresponds to a manganese content in the detergent composition of about 0.001% to 0.066% by weight, preferably about 0.0017% to 0.042% by weight based on the total weight of the detergent bleach composition. The molar ratio of complexing agent to manganese(III) in the catalyst is especially important and "effective amounts" of these ingredients connotes that such ratio be at least about 1:1, and preferably from about 10:1 to about 100:1; although ratios as high as 1000:1 can be used. It was found that the aforementioned ratio of complexing agent to manganese maintains the $Mn(III)$ in the complex as the active manganese species.

The action of the catalyst is believed to be due to the presence of a water-soluble complex of manganese(III) and a multidentate ligand wherein the complex catalyzes peroxide bleaching activity while inhibiting non-bleaching peroxide decomposition. Further, the multidentate ligand, which will be described in greater detail hereinbelow, imparts both hydrolytic and oxidative stability to the $Mn(III)$. This prevents the formation of water-insoluble manganese species such as MnO_2 , which tends to promote undesirable peroxide decomposition and stain fabrics through deposition as a precipitate.

A manganese(III) complex suitable for use in the present invention must meet the following three criteria:

1. It must be stable in a solution of the detergent bleach composition with respect to hydrolysis which would result in the formation of insoluble metal compounds at the alkaline pH's which are normally encountered in laundry wash water (hydrolytic stability);
2. It must be stable with respect to oxidation which would result in the formation of insoluble metal compounds at alkaline pH's in the presence of sodium hypochlorite, or other strongly oxidizing species which the user of the detergent bleach composition may choose to add to the wash water (oxidative stability); and
3. It must effectively catalyze peroxide bleaching activity.

Such complexes normally form homogeneous, non-colloidal solutions in alkaline aqueous systems.

Criterion (1) prevents formation of $MnO(OH)$, $Mn_2O_3 \cdot xH_2O$ and $Mn(OH)_2$; criterion (2) prevents formation of MnO_2 . Both $MnO(OH)/Mn(OH)_2/Mn_2O_3 \cdot xH_2O$ and MnO_2 are detrimental to $Mn(III)$ -catalyzed peroxide bleaching. Thus, at pH's of 9 to 12 which are normally encountered in aqueous wash media containing the detergent bleach composition of the invention, the water-soluble complex of $Mn(III)$ with the multidentate ligand catalyzes the bleaching activity of the peroxide compound while itself being stable to hydrolytic and oxidative degradation to water-insoluble manganese species.

Peroxide compounds suitable for use in the present invention include water-soluble inorganic persalts which yield hydrogen peroxide when dissolved in water. These include the alkali metal perborates, percarbonates, perphosphates and persulfates. Inorganic persalts which are available in the hydrated form are preferred in cases where they are more water-soluble than their anhydrous counterparts. Of the hydrated inorganic persalts, sodium perborate monohydrate is especially preferred.

Complexing agents, which are suitable for use as a source of multidentate ligands in the present invention by virtue of their ability to stabilize $Mn(III)$, are hydroxycarboxylic acids containing 5 or more carbon atoms, and the salts, hydrolyzable lactones, acid esters, ethers and boric esters thereof. A preferred group of the aforesaid hydroxycarboxylic acids can be represented by the general formula (I):



wherein R is CH_2OH , CHO or CO_2H ; n is from 3 to 8, preferably 4; and m is from 3 to n, preferably 4. Of these types of species, the alkali metal salts and especially the sodium salts are preferred. The hydroxycarboxylic compounds are stable at alkaline pH's (9-12) and have a hydroxyl group on each of the carbon atoms other than the carboxyl carbon; alternatively, the hydroxycarboxylic acid can have an aldehyde or carboxylic group on another carbon atom, and, in the case of straight-chain compounds, on the carbon atom farthest from the carboxyl carbon, and each of the remaining carbon atoms has a hydroxyl group. Examples of suitable hydroxycarboxylic acids are the hexonic hydroxyacids such as gluconic acid, gulonic acid, idonic acid and mannoic acid; the uronic acids such as glucuronic acid, galacturonic acid and mannuronic acid; the heptonic hydroxyacids such as glucoheptonic acid and its stereoisomers and mixture thereof; and sugars such as saccharic acid and isosaccharic acid.

The use of the foregoing complexing agents according to the present invention gives unexpected results in view of the fact that other, similar compounds such as malic acid, citric acid and tartaric acid and the related amine carboxylic acids such as EDTA do not impart the requisite hydrolytic and oxidative stability to the $Mn(III)$. Apparently there is a delicate balance between $Mn(III)$ stability and instability in these systems.

In another aspect, the present invention provides a bleaching agent composition containing (a) a peroxide compound having a bleaching action; and (b) a catalyst for the bleaching action of the peroxide compound, said catalyst comprising the aforesaid water-soluble complex of manganese(III) with a multidentate ligand.

The invention also embodies a method for preparing the catalyst for the bleaching action of the peroxide compound, which comprises:

(a) preparing an aqueous solution of a precursor of $Mn(III)$, e.g. a manganese(II) salt, and a multidentate ligand-supplying complexing agent wherein the molar ratio of the complexing agent to manganese is at least about 1:1;

(b) adjusting the solution prepared in step (a) to a pH of about 9 to 12; and

(c) when the $Mn(III)$ precursor is a $Mn(II)$ salt, agitating the solution in step (b) in air to oxidize the $Mn(II)$ selectively to $Mn(III)$, whereby a water-soluble complex of manganese(III) with the multidentate ligand is formed.

More particularly, the catalyst can be formed by preparing a neutral (pH about 7) solution of the desired complexing agent, e.g. sodium gluconate, and a precursor of $Mn(III)$, viz. a manganese(II) salt, typically a $Mn(II)$ salt of an inorganic acid, such as $MnCl_2$, $Mn(NO_3)_2$, $Mn_2(PO_4)_3$ and $MnSO_4$, and preferably manganese(II) sulphate. (Another precursor of $Mn(III)$ is $Mn(IV)$, which is the form in which complexed manganese such as the gluconate complex exists at pH greater than about 13 and which becomes converted to $Mn(III)$ when the pH is lowered to within the range of between about 9 and 12). The amount of complexing agent relative to the $Mn(II)$ salt is at least an equimolar amount, and preferably a 10-to 100-fold molar excess of the complexing agent is used. The pH of the solution is adjusted to between about 9 and about 12, preferably between 10 and 11, by adding, e.g., sodium hydroxide, and the solution is stirred in air as a source of oxygen. Oxidation of $Mn(II)$ to $Mn(III)$ occurs with rapid complexation of $Mn(III)$ with the ligand-supplying complexing agent. If a solid composition is desired, the solution can be evaporated to dryness by means well known to those skilled in the art. Alternatively, the catalyst can be formed by dissolving the desired

complexing agent in an aqueous solution of a Mn(III) salt, for example, manganese(III) acetate which is commercially available. The pH of the system is adjusted to about 10, e.g. by addition of 1N NaOH. The solution is evaporated to dryness to obtain a solid complex of Mn(III) with ligand supplied by the complexing agent. The stoichiometries of the manganese(III) salt and complexing agent are determined by the desired ratio of complexing agent to Mn(III).

In its preferred embodiments, the invention uses an aqueous solution containing manganese(II) sulphate and, as the complexing agent, sodium gluconate. The molar ratio of complexing agent to Mn(II) salt in the solution is from about 10:1 to 100:1. The pH is adjusted to about 10 using aqueous sodium hydroxide, and the bleach catalyst composition is obtained as a substantially dry, free-flowing solid powder or granular product by removing the water from the oxidized solution. This can be done conveniently by vacuum evaporation.

The bleach catalyst is compatible with common detergent builders such as carbonates, phosphates, silicates and aluminosilicates, e.g. zeolites. Carbonates, e.g. sodium carbonate, can be present in the detergent composition in amounts from 1% to 50% by weight; the upper limit is defined only by formulation constraints. Zeolites, e.g. Zeolite 4A, can be added at levels of 5% to 25% by weight, as can sodium tripolyphosphate or orthophosphate, and sodium silicates commonly used in detergents, e.g. wherein the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio ranges from 1:1 to 3.5:1. This allows for the control of wash water hardness so that detergency can be maximized. Furthermore, the bleach catalyst is effective in the presence of common sequestrants such as EDTA, DETPA or amino trimethylene phosphonic acid pentasodium salt (Dequest 2008). These can be added typically at levels of about 0.05% to about 0.3% by weight and, at these levels, catalytic bleaching activity is not adversely affected. Examples of organic builders are alkylmalonates, alkylsuccinates, polyacrylates, nitrilotriacetates (NTA), citrates, carboxy methyloxy malonates and carboxy methyloxy succinates.

As indicated above, the detergent bleach compositions of the present invention contain a surface-active agent or surfactant, generally in an amount of from about 2% to 50% by weight, preferably from 5% to 30% by weight. The surface-active agent can be anionic, nonionic, cationic or zwitterionic or a mixture of such agents.

Nonionic surfactants suitable for use in the present invention include water-soluble compounds produced by the condensation of ethylene oxide with a hydrophobic compound such as an alcohol, alkyl phenol, polypropoxy glycol or polypropoxy ethylene diamine. Also suitable are alkyl amine oxides, alkyl polyglucosides and alkyl methylsulphoxides. Preferred nonionic surfactants are polyethoxy alcohols formed as the condensation products of 1 to 30 moles of ethylene oxide with 1 mole of ethylene oxide with 1 mole of branched-or straight-chain, primary or secondary aliphatic alcohols having from about 8 to about 22 carbon atoms; more especially, 6 to 15 moles of ethylene oxide are condensed with 1 mole of straight-or branched-chain, primary or secondary aliphatic alcohol having from about 10 to about 16 carbon atoms. Certain polyethoxy alcohols are commercially available under the trade-names "Neodol", "Synperonic" and "Tergitol".

Anionic surfactants suitable for use in formulating the detergent bleach compositions of the invention include water-soluble alkali metal alkylbenzenesulphonates, alkyl sulphates, alkylpolyethoxyether sulphates, paraffin sulphonates, alpha-olefin sulphonates, alpha-sulphocarboxylates and their esters, alkylglyceryl ether sulphonates, fatty acid monoglyceride sulphates and sulphonates, alkylphenolpolyethoxy ethersulphates, 2-acyloxyalkane-1-sulphonates and beta-alkyloxyalkane sulphonates. Soaps can also be used as anionic surfactants. Preferred anionic surfactants are alkylbenzenesulphonates with about 9 to about 15 carbon atoms in a linear or branched alkyl chain, more especially about 11 to about 13 carbon atoms; alkylsulphates with about 8 to about 22 carbon atoms in the alkyl chain, more especially from about 12 to about 18 carbon atoms; alkylpolyethoxy ethersulphates with about 10 to about 18 carbon atoms in the alkyl chain and an average of about 1 to about 12 $-\text{CH}_2\text{CH}_2\text{O}-$ groups per molecule; linear paraffin sulphonates with about 8 to about 24 carbon atoms, more especially from about 14 to about 18 carbon atoms and alpha-olefin sulphonates with about 10 to about 24 carbon atoms, more especially about 14 to about 16 carbon atoms; and soaps having from 8 to 24, especially 12 to 18 carbon atoms.

Cationic surface-active agents suitable for use in the invention include the quaternary ammonium compounds, e.g. cetyltrimethylammonium bromide or chloride and distearyldimethylammonium bromide or chloride, and the fatty alkyl amines.

Zwitterionic surfactants that can be used in the present invention include water-soluble derivatives of aliphatic quaternary ammonium, phosphonium and sulphonium cationic compounds in which the aliphatic moieties can be straight or branched, and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water-solubilizing group, especially alkyldimethylammonium propanesulphonates and carboxylates (betaines) and alkyldimethylammoniohydroxy propanesulphonates and carboxylates wherein the alkyl group in both types contains from about 8 to 18 carbon atoms.

Typical listings of the classes and species of surfactants useful in this invention appear in "Surface Active Agents", Vol. I, by Schwartz & Perry (Interscience 1949) and "Surface Active Agents", Vol. II, by Schwartz, Perry & Berch (Interscience 1958). These listings, and the foregoing recitation of specific surfactant compounds and mixtures can be used in formulating the detergent bleach composition of the present invention.

Other components/adjuncts commonly used in detergent compositions and which can be used in the instant detergent bleach compositions include soil-suspending agents/incrustation inhibitors, such as water-soluble salts of carboxymethylcellulose, carboxyhydroxymethylcellulose, copolymers of maleic anhydride and vinyl ethers, copolymers of maleic acid (anhydride) and (meth)acrylic acid, polyacrylates and polyethylene glycols having a molecular weight of about 400 to 10,000 or more. These can be used at levels of about 0.5% to about 10% by weight.

Dyes, pigments, optical brighteners, perfumes, anti-caking agents, suds control agents, enzymes and fillers can also be added in varying amounts as desired.

Enzymes which can be used herein include proteolytic enzymes, amylolytic enzymes and lipolytic enzymes (lipases). Various types of proteolytic enzymes and amylolytic enzymes are known in the art and are commercially available.

Particularly suitable lipases are those lipases which show a positive immunological cross-reaction with the antibody of the lipase produced by the micro-organism Pseudomonas fluorescens IAM 1057, as described in EP-A-0206390.

Another class of particularly suitable lipases is that of fungal lipases produced by Hemicula lanuginosa, Thermomyces lanuginosus, and bacterial lipases which show a positive immunological cross-reaction with the antibody of the lipase produced by the micro-organism Chromobacter viscosum var. lipolyticum NRRL B-3673.

Typical examples of such bacterial lipases are the lipase ex Pseudomonas fluorescens IAM 1057 available from Amano Pharmaceutical Co., Nagoya, Japan, under the trade-name Amano-P lipase, the lipase ex Pseudomonas fragi FERM P-1339 (available under the trade-name Amano-B), lipase ex Pseudomonas nitroreducens var. lipolyticum FERM P-1338 (available under the trade-name Amano-CES), lipases ex Chromobacter viscosum var. lipolyticum NRRL B-3673, commercially available from Toyo Jozo Co., Tagata, Japan; and further Chromobacter viscosum lipases from U.S. Biochemical Corp., U.S.A. and Diosynth Co., The Netherlands; and lipases ex Pseudomonas gladioli. A fungal lipase ex Hemicula lanuginosa is for example available from Amano under the trade-name Amano-CE.

Fabric-softening agents, both cationic and nonionic in nature, as well as clays, e.g. bentonite, can also be added to provide softening-in-the-wash properties.

The detergent compositions of the invention are preferably formulated as free-flowing particles, e.g. in powdered or granular form, and can be produced by any of the conventional techniques employed in the manufacture of detergent compositions, but preferably by slurry-making and spray-drying processes to form a detergent base powder to which heat-sensitive ingredients, including the peroxide bleaching agent and optionally some other ingredients as desired, and the bleach catalyst, can be added as dry substances. Alternatively, a liquid catalyst solution can be added separately to a wash/bleach water containing the peroxide bleaching agent.

The invention will now be illustrated by the following non-limiting examples.

Example I

In a typical run, 0.338 g MnSO₄ and 21.8 g sodium gluconate are dissolved in 500 ml doubly distilled water. Addition of 2 ml of 1N sodium hydroxide raises the pH to 10 and the solution turns from colourless to honey brown. The solution is placed on a rotary evaporator to remove the water, then freeze-dried to a light tan powder. The catalyst mixture thus produced is used in the detergent bleach formulations illustrated in Examples II and III, below.

Example II

The following detergent bleach composition is formulated

<u>Component</u>	<u>% by weight</u>
Neodol 45-13 (a C ₁₄ -C ₁₅ linear primary alcohol ethoxylate (13 EO))	6.4
sodium carbonate	25.0
sodium silicate	7.5
sodium hydroxide	0.5
sodium sulphate	29.0
sodium perborate monohydrate	20.0
catalyst	10.0
water to 100%	

The composition is tested at a dosage of 2 g/l (1 ppm manganese) in a 15-minute wash at 40°C. The bleaching effect on tea-stained cloth measured by ΔR (the change in reflectance between washed and unwashed cloth) at various degrees of water hardness is given in Table I.

Table I

<u>Hardness (FH)*</u>	<u>ΔR</u>
2°	12.0
6°	11.6
12°	10.5
15°	10.3
18°	8.3
24°	4.8

* Hardness as French hardness (FH); 1° FH = 10 ppm
2Ca²⁺/1Mg²⁺ calculated as CaCO₃.

The composition is tested at a series of wash water concentrations spanning the effective dosage range of 0.1 to 4 ppm Mn(III) in a 15-minute wash at 40°C at a constant initial water hardness of 12° FH. The bleaching effects on tea-stained cloth measured by delta R are given in Table II.

Table II

	<u>ppm Mn(III)</u>	<u>ΔR</u>
5	0	1.4
	0.2	3.9
10	0.4	6.2
	0.6	7.2
	0.8	6.9
15	1.2	7.7
	1.5	7.6
	2.0	6.8
20	4.0	4.0
	5.0	0.8

Example III

25 The following detergent bleach composition is formulated.

	<u>Component</u>	<u>% by weight</u>
	sodium C ₁₂ alkybenzenesulphonate	9.6
	Neodol 45-13	3.2
30	sodium carbonate	40.9
	sodium tripolyphosphate	5.8
	sodium silicate	2.9
35	sodium hydroxide	1.1
	Dequest 2006	1.2
	sodium perborate monohydrate	23.4
40	catalyst	11.7

The composition is tested at a series of 40°C wash water concentrations spanning the effective dosage range of 0.1 to 4 ppm Mn(III) for 15 minutes each. Table III shows the change in reflectance (ΔR) of tea-stained cloth as a function of manganese concentration at an initial water hardness of 9° FH.

Table III

	<u>ppm Mn(III)</u>	<u>ΔR</u>
5	0.0	1.6
	0.2	4.1
	0.4	5.7
10	0.6	7.2
	0.8	8.8
	1.0	9.6
15	1.5	11.1
	2.0	11.8
	2.4	8.1
20	3.1	7.2
	3.5	2.4
	4.0	2.0
25	5.0	0.5

Example IV

The following detergent composition A (without perborate or catalyst) is formulated:

	<u>Component</u>	<u>% by weight</u>
30	sodium C ₁₂ alkybenzenesulphonate	9.6
	Neodol 45-13	3.2
35	sodium carbonate	40.9
	sodium tripolyphosphate	5.8
	sodium silicate	2.9
	sodium hydroxide	1.1
40	Dequest 2006	1.2
	sodium sulphate (filler)	35.1

The following detergent composition B (without catalyst) is formulated:

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	<u>Component</u>	<u>% by weight</u>
	sodium C ₁₂ alkybenzenesulphonate	9.6
	Neodol 45-13	3.2
5	sodium carbonate	40.9
	sodium tripolyphosphate	5.8
	sodium silicate	2.9
10	sodium hydroxide	1.1
	Dequest 2006	1.2
	sodium perborate monohydrate	23.4
15	sodium sulphate	11.7

The following detergent composition IV (with perborate and catalyst) is formulated:

	<u>Component</u>	<u>% by weight</u>
20	sodium C ₁₂ alkybenzenesulphonate	9.6
	Neodol 45-13	3.2
	sodium carbonate	40.9
25	sodium tripolyphosphate	5.8
	sodium silicate	2.9
	sodium hydroxide	1.1
	Dequest 2006	1.2
30	sodium perborate monohydrate	23.4
	catalyst	11.7

Table IV shows the change in reflectance of wine-stained cloth using the formulations A, B and IV each at an initial water hardness of 12°FH.

Table IV

	<u>Composition</u>	<u>Δ R</u>
40	A (without perborate or catalyst)	11.6
	B (without catalyst)	18.8
45	IV (with perborate and catalyst)	25.1

Table IV demonstrates the benefit of the added peroxide bleaching agent and the further benefit which may be obtained through use of the catalyst.

50 Example V

Hydrolytic stability of the catalysts of the invention is defined in terms of the water-solubility of the manganese at a pH of 10 to 11. Oxidative stability is defined in terms of the water-solubility of manganese at a pH of 10 to 11 in the presence of strong oxidizing agents such as hypochlorite. Stability tests are run at a mole ratio of 10 ligand/1 Mn²⁺ (0.5 mmol ligand/0.05 mmol Mn²⁺). The pH is raised to 11 with 1N NaOH and the solution is allowed to stand at room temperature for 30 minutes. If the solution remains homogeneous, then 5 mmol hypochlorite is added and the system is allowed to stand for 2 hours.

Table V

	<u>Ligand</u>	<u>Hydrolytic Stability</u>	<u>Oxidative Stability</u>
5	picolinic acid	no	--
	NTA	yes	no
	Dequest 2006	yes	no
10	Dequest 2041*	yes	no
	EDTA	yes	no
	gluconate	yes	yes
15	glucoheptonate	yes	yes
	Tiron**	yes	no
	polyacrylic acid (MW = 2400)	yes	no
20	sulphosalicylic acid	no	--
	saccharic acid	yes	yes
	DETPA	yes	no
	quinic acid	yes	yes
25	glucouronic acid	yes	yes
	galactouronic acid	yes	yes
	gulonic acid	yes	yes
30	* Dequest 2041 = Ethylenediaminetetra(methylene- phosphonic acid).		
35	** Tiron = 4,5-dihydroxy-1,3-benzenedisulphonic acid disodium salt monohydrate.		

From the data in Table V it can be seen that quinic acid meets the requirement for hydrolytic and oxidative stability and is suitable for use according to the present invention, even though it differs in chemical structure from the general class of suitable complexing agents which are hydroxycarboxylic acids containing at least 5 carbon atoms according to formula I above.

Examples VI-VIII

The following detergent bleach compositions were prepared:

	<u>Composition</u>	<u>% by weight</u>	
		<u>VI</u>	<u>VII</u>
5	sodium C ₁₂ alkylbenzenesulphonate	7.7	11.0
10	C ₁₁ -C ₁₃ branched alcohol/7 ethylene oxide	3.4	4.0
	sodium stearate	3.4	-
	sodium carbonate, anhydrous	35.0	30.0
15	calcite	20.0	20.0
	sodium silicate	4.6	8.0
	sucrose	4.0	4.0
20	sodium sulphate	2.1	-
	sodium carboxymethylcellulose (SCMC)	0.5	0.5
	ethylene diamine tetraacetate (EDTA)	0.2	0.1
25	fluorescer	0.1	0.2
	sodium perborate monohydrate	15.0	15.0
	water to 100%		

	<u>Composition VIII</u>	<u>% by weight</u>	
30	sodium C ₁₂ alkylbenzenesulphonate	9.0	
	nonionic/7 ethylene oxide	1.0	
35	nonionic/3 ethylene oxide	3.0	
	Zeolite 80 (10% H ₂ O)	24.2	
	polymer structurant	4.2	
40	sodium sulphate	28.0	
	sodium carbonate	2.4	
	sodium silicate	4.0	
45	sodium perborate monohydrate	15.0	
	water + minors to 100%		

Bleaching experiments were carried out in a 40°C thermostated jacketed glass beaker containing 1 litre demineralized water adjusted to a water hardness of 27° FH. A dosage of 6 g/l of each composition was used in all experiments. When catalyst was added, this was dosed at 1.5 ppm manganese.

The catalyst used was manganese(III) gluconate composed of a 10:1 molar ratio of gluconate to manganese.

The bleaching results on the tea-stained test cloths measured as ΔR are given in the following Tables VII-VIII.

Tables

Time (minutes)	VI (pH 10.4)		VII (pH 10.4)		VIII (pH 10.05)	
	(-Mn)	(+Mn)	(-Mn)	(+Mn)	(-Mn)	(+Mn)
	ΔR	ΔR	ΔR	ΔR	ΔR	ΔR
15	1.8	10.0	3.0	8.7	0.9	4.7
30	7.7	17.5	10.6	15.4	3.3	13.2
45	15.9	22.3	16.1	19.6	6.8	17.9
60	16.2	23.1	19.0	21.2	10.7	20.1

The above tables again demonstrate the clear benefit obtained through the use of the catalyst.

Example IX

In the following Example the effect of water hardness on peroxide bleaching of tea-stained test cloths using Mn(III) gluconate-catalyzed, zeolite-based composition of Example VIII was compared with a non-catalyzed zeolite-based composition.

Washing experiment conditions:

- 1) Dosage 6 g/l
- 2) Initial pH 10.8
- 3) Heat up from 20°C to 40°C in 13 minutes and maintain at this temperature for 37 minutes
- 4) 0.5 ppm Mn
- 5) Final pH 10.1.

The bleaching results are given in the following Table IX(1) and Table IX(2).

Table IX(1)

Water hardness (°FH)	0	16	27	36	54
Mn (ppm)	0.5	0.5	0.5	0.5	0.5
ΔR	13.1	15.3	18.1	18.0	18.2

Table IX(2)

Water hardness (°FH)	0	15	27	40
Mn (ppm)	-	-	-	-
ΔR	10.1	11.1	10.1	10.4

Example X

This Example shows dose response of the Mn(III) gluconate on peroxide bleaching of the tea-stained test cloths using zeolite-based composition of Example VIII.

Washing conditions:

- 1) Dosage 6 g/l
- 2) Initial pH 10.6
- 3) Water hardness 27°FH
- 4) Heat up from 20°C to 40°C as in Example IX
- 5) Varying dosage of the Mn(III) gluconate.

The bleaching results are given in the following Table X.

Table X

Mn (ppm)	0	0.075	0.15	0.25	0.5	0.75	1.0	1.25	1.5
ΔR	11.2	15.8	16.4	17.7	18.1	18.6	17.4	19.9	16.9

Example XI

Six catalyst solutions were prepared consisting of 0.01 M Mn^{2+} /0.25 M gluconate, 0.01 M Mn^{2+} /0.25 M glucoheptonate, 0.01 M Fe^{2+} /0.02 M gluconate/0.015 M EDTA, 0.01 M Fe^{2+} /0.02 M gluconate, 0.01 M Fe^{2+} /0.02 M glucoheptonate/0.015 M EDTA, 0.01 M Fe^{2+} /0.02 M glucoheptonate. The solutions were prepared in the following manner.

Manganese(III) gluconate was prepared by mixing 0.169 g $MnSO_4 \cdot H_2O$ and 5.453 g sodium gluconate with 50 mls doubly distilled water. After a homogeneous solution was obtained, the pH of the solution was adjusted to 10 with the addition of 1 N NaOH. The final volume was adjusted to 100 mls with doubly distilled water. Manganese(III) glucoheptonate was similarly prepared using 5.204 g of glucoheptonic acid-gamma-lactone.

Iron(II) glucoheptonate was prepared according to European patent application N° 0 124 341. A 40 ml solution containing 0.1390 g $FeSO_4 \cdot 7H_2O$, 0.2081 g glucoheptonic acid-gamma-lactone and 0.3257 g $Na_2EDTA \cdot 3H_2O$ (EDTA = ethylenediaminetetraacetic acid) in doubly distilled water was prepared. The pH was raised to 11.5 with 1 N NaOH and diluted to a final volume of 50 mls with doubly distilled water. Iron(III) gluconate was prepared in a similar manner using 0.2780 g $FeSO_4 \cdot 7H_2O$, 0.4363 g sodium gluconate and 0.6513 g $Na_2EDTA \cdot 3H_2O$ in a final volume of 100 mls. Both catalysts were also prepared in the absence of EDTA.

Bleaching experiments were carried out in a Terg-otometer set at 40°C. One litre of doubly distilled water containing 120 ppm hardness (2 Ca^{2+} /1 Mg^{2+}) solution was used. Agitation was for 15 minutes, followed by 2 minutes cold water rinse. The cloths used were tea-stained test cloths and two swatches were washed per pot. The ingredients used were 1.1 g detergent base powder, 0.1 g sodium carbonate, 0.4 g sodium perborate monohydrate and the appropriate amount of catalyst solution to deliver 1 or 2 ppm Mn or Fe. The composition of the base powder was:

	<u>% by weight</u>
sodium C_{12} alkybenzenesulphonate	14.8
nonionic alkoxylate	4.9
sodium carbonate	63.3
sodium tripolyphosphate	8.9
sodium silicate	4.5
sodium hydroxide	1.7
Dequest 2006	1.9

The bleaching results are given in the following Table XI.

Table XI

	<u>Run</u>	<u>Perborate</u> (g)	<u>Catalyst</u>	<u>Concentration</u> (M ⁿ⁺) ppm	<u>Δ R</u>
5	1	-	-	-	-2.9
	2	0.4	-	-	1.3
10	3	0.4	Mn/gluconate	1	9.0
	4	0.4	Fe/gluconate/EDTA	1	-0.5
	5	0.4	Fe/gluconate	1	-0.3
15	6	0.4	Mn/gluconate	2	10.1
	7	0.4	Fe/gluconate/EDTA	2	-1.3
	8	0.4	Fe/gluconate	2	-0.1
20	9	0.4	Mn/glucoheptonate	1	9.3
	10	0.4	Fe/glucoheptonate/EDTA	1	0.8
	11	0.4	Fe/glucoheptonate	1	0.3
	12	0.4	Mn/glucoheptonate	2	9.2
25	13	0.4	Fe/glucoheptonate/EDTA	2	-0.9
	14	0.4	Fe/glucoheptonate	2	-0.3

From the above Table it is clear that the manganese catalysts according to the invention (Run 3, 6, 9 and 12) exert a significant enhancement of the bleach performance at 40°C, whereas all the iron complexes with similar ligands are ineffective or even detrimental to the perborate bleaching performance (Run 4, 5, 7, 8, 10, 11, 13 and 14).

Claims

1. A bleaching composition containing:

(a) a peroxide compound selected from the group consisting of inorganic persalts which when in water yield hydrogen peroxide; and

(b) a catalyst for the bleaching action of the peroxide compound, comprising a complex of manganese(III) and a multidentate ligand supplied by a complexing agent selected from the group consisting of hydroxycarboxylic acids containing at least 5 carbon atoms and the salts, lactones, acid esters, ethers and boric esters thereof, and wherein the molar ratio of complexing agent to manganese is at least about 1:1.

2. A composition according to claim 1,

characterized in that the inorganic persalt is alkali metal perborate, percarbonate, perphosphate or persulfate or mixture thereof.

3. A composition according to claim 1,

characterized in that the hydroxycarboxylic acid possesses a hydroxyl group on each of the carbon atoms other than the carboxyl carbon.

4. A composition according to claim 1,

characterized in that the hydroxycarboxylic acid is a straight-chain acid having an aldehyde or carboxylate group on the carbon atom farthest from the carboxyl carbon and each of the remaining carbon atoms other than the carboxyl carbon has a hydroxyl group.

5. A composition according to claim 1,

characterized in that the hydroxycarboxylic acid is a hexonic hydroxyacid selected from the group consisting of gluconic acid, gulonic acid, idonic acid and mannoic acid.

6. A composition according to claim 1,
characterized in that the hydroxycarboxylic acid is a uronic acid selected from the group consisting of glucuronic acid, galactouronic acid and mannuronic acid.
7. A composition according to claim 1,
6 characterized in that the hydroxycarboxylic acid is a heptonic hydroxyacid selected from the group consisting of glucoheptonic acid and its stereoisomers.
8. A composition according to claim 1,
characterized in that the hydroxycarboxylic acid is a sugar selected from the group consisting of saccharic acid and isosaccharic acid.
- 10 9. A composition according to any of the above claims 1-8, characterized in that it further comprises:
(c) a surface-active agent selected from the group consisting of nonionic, anionic, cationic and zwitterionic detergents and mixtures thereof; and
(d) a detergent builder.
10. A composition according to claim 9,
15 characterized in that
the surface-active agent is present in about 2% to about 50% by weight of the composition;
the detergent builder is present in about 1% to the detergent builder is present in about 2% to about 85% by weight of the composition;
the peroxide compound is present in about 5% to about 30% by weight of the composition; and
20 the catalyst is present in an amount such that the manganese content is about 0.001% to about 0.2 of the weight of the composition.
11. A composition according to claim 10,
characterized in that the peroxide compound is present in about 15% to about 25% by weight and the catalyst is present in an amount such that the manganese content is about 0.0017% to about 0.125% by
25 weight of the composition.
12. A catalyst for the bleaching action of peroxide compounds in the (detergent) bleach composition according to the above claims 1-11, comprising a complex of manganese(III) and a multidentate ligand supplied by a complexing agent selected from the group consisting of hydroxycarboxylic acids containing at least 5 carbon atoms and the salts, lactones, acid esters, ethers and boric esters thereof, and wherein the
30 molar ratio of complexing agent to manganese is at least about 1:1.
13. A catalyst according to claim 12,
characterized in that the hydroxycarboxylic acid possesses a hydroxyl group on each of the carbon atoms other than the carboxyl carbon.
14. A catalyst according to claim 12,
35 characterized in that the hydroxycarboxylic acid is a straight-chain acid having an aldehyde or carboxylate group on the carbon atom farthest from the carboxyl carbon and each of the remaining carbon atoms other than the carboxyl carbon has a hydroxyl group.
15. A catalyst according to claim 12,
characterized in that the hydroxycarboxylic acid is a hexonic hydroxyacid selected from the group
40 consisting of gluconic acid, gulonic acid, idonic acid and mannoic acid.
16. A catalyst according to claim 12,
characterized in that the hydroxycarboxylic acid is a uronic acid selected from the group consisting of glucouronic acid, galactouronic acid and mannuronic acid.
17. A catalyst according to claim 12,
45 characterized in that the hydroxycarboxylic acid is a heptonic hydroxyacid selected from the group consisting of glucoheptonic acid and its stereoisomers.
18. A catalyst according to claim 12,
characterized in that the hydroxycarboxylic acid is a sugar selected from a group consisting of saccharic acid and isosaccharic acid.
- 50 19. A catalyst according to claim 12,
characterized in that the hydroxycarboxylic acid is quinic acid.
20. A method for preparing the catalyst of claims 12-19, comprising the steps of:
(a) preparing an aqueous solution of (i) a source of manganese(III) and (ii) a multidentate ligand-supplying complexing agent wherein the molar ratio of the complexing agent to manganese is at least about
55 1:1;
(b) adjusting the solution prepared in step (a) to a pH of between about 9 and about 12; and
(c) agitating the solution obtained in step (b) in air to form a water-soluble complex of manganese(III) with the multidentate ligand.

21. A method according to claim 20, characterized in that the source of manganese(III) is a manganese(II) salt.

22. A method according to claim 21, characterized in that:

the manganese(II) salt is manganese(II) sulphate;

5 the complexing agent is sodium gluconate; and

the pH is adjusted in step (b) to a pH of about 10 using sodium hydroxide.

23. A method according to any one of the claims 20-22, characterized in that the molar ratio of the complexing agent to manganese is between about 10:1 and 100:1.

24. A method according to claims 20-23,
10 characterized in that the water is removed from the complex formed in step (c).

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